Caribbean sclerosponge radiocarbon measurements re-interpreted in terms of U/Th age models

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Abstract

Previously unpublished AMS radiocarbon measurements of a sclerosponge from tongue of the ocean (TOTO), Bahamas, as well as preliminary data from an investigation of the radiocarbon records of sclerosponges living at different depths in the adjacent Bahamas basin, Exuma Sound, are interpreted in terms of U-series age models. The data are compared to an existing Caribbean sclerosponge radiocarbon bomb curve measured using standard gas proportional beta counting and used to interpret a 210Pb age model. The Δ14C records from the sclerosponges illustrate a potential for use of radiocarbon both as a tracer of subsurface water masses or as an additional age constraint on recently sampled sclerosponges. By using an independent age model, this study lays the framework for utilizing sclerosponges from different locations in the tropics and subtropics and different depths within their wide depth range (0–250 m) to constrain changes in production of subtropical underwater in the Atlantic Ocean. This framework is significant because the proxy approach is necessary to supplement the short and coarse time series being used to constrain variability in the formation of Caribbean subtropical underwater, the return flow of a shallow circulation cell responsible for nearly 10% of the heat transported poleward in the N. Atlantic.

PACS: 91.65.Dt; 91.65.Fw; 92.10.Fj; 92.10.Fr; 92.70.Er

Keywords: Sclerosponge; Ceratoporella nicholsoni; Radiocarbon; U-series dating; N. Atlantic

1. Introduction

Sclerosponges have considerable use in paleoceanographic studies as archives of isotope and minor element proxies of temperature, salinity, and other environmental parameters [1–6]. In the Atlantic basin, the sclerosponge Ceratoporella nicholsoni can provide greater than 500 yr of continuously accreted skeletal material [1] representative of water masses as deep as 250 m and perhaps beyond [7]. Recently, sclerosponges from the Bahamas have been used to assess instrumental records of salinity change in the subtropical N. Atlantic using stable oxygen isotopes and Sr/Ca ratios over an extended time domain and at higher resolution than the instrumental record [4]. These salinity changes occur in the subsurface water mass known as the subtropical underwater (SUW) that mixes S. Atlantic and N. Atlantic salinity maximum water (SMW) in the subsurface Caribbean Sea. Despite recent advances and the paleoceanographic potential of the organism, no attempts have been made to use radiocarbon records archived in sclerosponges to trace water masses in the Caribbean.

As a tracer, radiocarbon can be used a proxy for the relative amount of N. Atlantic SMW in the Caribbean by exploiting the ∼40‰ difference between the N. Atlantic and S. Atlantic (Fig. 1 [8]). The relative contribution of N. Atlantic SMW to the Caribbean SUW is important because this forms the subsurface leg of the subtropical convection cell (STC) that re-emerges at the equator under Ekman pumping, regaining the heat lost at higher latitudes [9–13]. The surface pathways of the STC in the N. Atlantic are less well defined, however it is estimated to transport...
between 0.1 and 0.4 Wm⁻² of tropical heat poleward [13,14]. This is nearly 10% of the heat transported by the meridional over-turning cell (MOC) and its importance may manifest more in the interactions between the MOC and the STC in the N. Atlantic. Sclerosponges are unique in their ability to record changes in the STC conditions over time because of their depth range and habitat, and their lifespan and chemistry suggest that radiocarbon would be an ideal tracer to exploit from their skeletons. In addition, proxy data such as those recorded in scleractinian coral skeletons are the only method that can increase the time resolution of oceanic ¹⁴C records beyond that presented by the WOCE and CLIVAR time slices of observational data.

Sclerosponge radiocarbon data were first published [15] when interest in sclerosponge skeletons as proxy archives was originally piqued by their concentric bands and the Δ¹⁴C bomb curve was interpreted in terms of ⁰¹⁰⁴⁸Pb age estimates that stipulated a constant Pb/Ca ratio. The authors realized that this initial assumption was errant as the Pb/Ca fluctuations, brought on by increasing consumption of gasoline containing ethyl lead additives by automobiles, were concurrently being documented in marine carbonates [16–18]. Since then, Pb/Ca curves from sclerosponges have recently been used as first order tests of sclerosponge age models [2,19]. The age corrected Δ¹⁴C [20] data presented here are calculated in terms of the independent U-series radiometric chronometer and they indicate the reproducibility of the Δ¹⁴C bomb curve and the potential of age corrected Δ¹⁴C as an oceanographic tracer in sclerosponges where the age model is well confined.

2. Methods

The sclerosponge from TOTO (Fig. 1) was sampled by submersible at 143 m in 1990 and the sclerosponges from Exuma Sound were sampled between depths of 67 and 152 m by submersible in 1995 (data presented herein are from two specimens, 67 m and 136 m). Subsampling of all sclerosponge specimens was carried out by drilling at a low speed with a diamond coated abrasive dental bur of approximately 0.5 mm width (Fig. 2). The TOTO sclerosponge was subsampled from individual concentric bands in a non-continuous fashion, attempting to minimize the amount of powder sampled from adjacent bands. The Exuma sclerosponges were subsampled in a continuous fashion with the top (closest to the surface of the sclerosponge) and bottom of each sample measured perpendicular to the concentric banding (Fig. 2). Drilling of carbonate material has been alleged to cause mobilization of carbon between the mineral phase, trapped organic material, and that present in the atmosphere although debate over the exact affects of drill stress on carbonate samples, if any, has not been conclusive [21–25]. Sclerosponges are difficult to subsample by chipping entire pieces from the skeleton due to their density, therefore a low speed drill technique was employed to minimize stress from the drill without sacrificing sampling accuracy.

Aragonite powder generated by drilling was stored in sealed vials which were kept in dessicators until analysis.
Samples from the TOTO sclerosponge were analyzed at the NSF-Arizona AMS facility between 1992 and 1995. Samples from the Exuma sclerosponges were analyzed at the national ocean sciences accelerator mass spectrometer at Woods Hole Oceanographic Institution in 2005. This is in contrast to the earlier radiocarbon data from Benavides and Druffel [15] which were analyzed by counting techniques.

Sclerosponge subsamples analyzed for $^{238}$U, $^{234}$U, $^{232}$Th and $^{230}$Th were prepared by cutting pieces of sclerosponge from the skeleton using concentric bands as a sampling template. The skeletons were cut using a diamond band saw. Subsamples were analyzed by thermal ionization mass spectrometry (TIMS) by Anton Eisenhauer and his group at IFM/Geomar in Kiel, Germany. The specific methods, the data and their interpretations are discussed elsewhere in further detail [19,26].

3. Results

A summary of the U-series age models with associated statistical uncertainties is shown in Table 1, and all $^{14}$C data are shown in Table 2. The initial results from the TOTO sclerosponge analyzed at the NSF-Arizona AMS Facility are shown in Fig. 3. Large errors persist due to the small size of the samples submitted. Similarly sized samples were analyzed from the Exuma Sound sclerosponges (Fig. 3), however they were analyzed in 2005, when the TOTO sclerosponge analyzed at the NSF-Arizona AMS facility between 1992 and 1995. Samples from the Exuma Sound sclerosponges were analyzed at the Arizona NSF AMS facility. Recently other sclerosponges from near the same location have been analyzed at WHOI-NOSAMS (green and blue). These data are all compared to standard gas proportional beta counting radiocarbon data from a sclerosponge in the central Caribbean (Chalet Caribe and Jamaica) [15]. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

<table>
<thead>
<tr>
<th>Sclerosponge</th>
<th>Depth (m)</th>
<th>Collected A.D.</th>
<th>Analyzed A.D.</th>
<th>U/Th growth rate, $r$ (µm/yr)</th>
<th>Surface age (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSI-16</td>
<td>67</td>
<td>1995</td>
<td>2002</td>
<td>241 (±70)</td>
<td>7 (±1)</td>
</tr>
<tr>
<td>LSI-20</td>
<td>136</td>
<td>1995</td>
<td>2002</td>
<td>144 (±28)</td>
<td>7 (±1)</td>
</tr>
<tr>
<td>TOTO</td>
<td>146</td>
<td>1990</td>
<td>2002</td>
<td>137 (±25)</td>
<td>12 (±1)</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Requisition #</th>
<th>Sequence #</th>
<th>Sample</th>
<th>Depth (m)</th>
<th>Skeletal distance (mm)</th>
<th>U/Th age (yr)</th>
<th>Fm</th>
<th>$\delta^{13}$C (%o VPDB)</th>
<th>$\delta^{14}$C (%o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13774</td>
<td>1</td>
<td>TOTO</td>
<td>143</td>
<td>1.5 (±1)</td>
<td>11 (±8)</td>
<td>0.9458 (±0.0069)</td>
<td>3.99</td>
<td>-51 (±7)</td>
</tr>
<tr>
<td>13776</td>
<td>2</td>
<td>TOTO</td>
<td>143</td>
<td>34 (±1)</td>
<td>248 (±46)</td>
<td>0.935 (±0.0085)</td>
<td>4.67</td>
<td>-88 (±10)</td>
</tr>
<tr>
<td>14560</td>
<td>3</td>
<td>TOTO</td>
<td>143</td>
<td>19 (±1)</td>
<td>139 (±26)</td>
<td>0.9381 (±0.0068)</td>
<td>4.71</td>
<td>-73 (±8)</td>
</tr>
<tr>
<td>14561</td>
<td>4</td>
<td>TOTO</td>
<td>143</td>
<td>15 (±1)</td>
<td>109 (±21)</td>
<td>0.9485 (±0.0067)</td>
<td>6.64</td>
<td>-59 (±7)</td>
</tr>
<tr>
<td>16504</td>
<td>5</td>
<td>TOTO</td>
<td>143</td>
<td>30 (±1)</td>
<td>219 (±41)</td>
<td>0.882 (±0.029)</td>
<td>4.64</td>
<td>-137 (±30)</td>
</tr>
<tr>
<td>16505</td>
<td>6</td>
<td>TOTO</td>
<td>143</td>
<td>27 (±1)</td>
<td>197 (±37)</td>
<td>0.9117 (±0.0094)</td>
<td>4.61</td>
<td>-106 (±10)</td>
</tr>
<tr>
<td>16506</td>
<td>7</td>
<td>TOTO</td>
<td>143</td>
<td>20 (±1)</td>
<td>146 (±28)</td>
<td>0.917 (±0.011)</td>
<td>4.67</td>
<td>-95 (±11)</td>
</tr>
<tr>
<td>16507</td>
<td>8</td>
<td>TOTO</td>
<td>143</td>
<td>15 (±1)</td>
<td>109 (±21)</td>
<td>0.922 (±0.031)</td>
<td>4.64</td>
<td>-86 (±31)</td>
</tr>
<tr>
<td>16508</td>
<td>9</td>
<td>TOTO</td>
<td>143</td>
<td>9 (±1)</td>
<td>66 (±14)</td>
<td>0.889 (±0.073)</td>
<td>4.01</td>
<td>-114 (±73)</td>
</tr>
<tr>
<td>5030*</td>
<td>10</td>
<td>LSI-16</td>
<td>67</td>
<td>9.5 (±1)</td>
<td>39 (±11)</td>
<td>0.9524 (±0.0032)</td>
<td>4.68</td>
<td>-47 (±3)</td>
</tr>
<tr>
<td>5030*</td>
<td>11</td>
<td>LSI-20</td>
<td>136</td>
<td>10.5 (±1)</td>
<td>73 (±16)</td>
<td>0.95855 (±0.0051)</td>
<td>4.71</td>
<td>-45 (±5)</td>
</tr>
<tr>
<td>5030*</td>
<td>12</td>
<td>LSI-20</td>
<td>136</td>
<td>6.5 (±1)</td>
<td>45 (±11)</td>
<td>0.9519 (±0.004)</td>
<td>4.6</td>
<td>-48 (±4)</td>
</tr>
<tr>
<td>5030*</td>
<td>13</td>
<td>LSI-20</td>
<td>136</td>
<td>1.5 (±1)</td>
<td>10 (±7)</td>
<td>1.1408 (±0.0046)</td>
<td>4.3</td>
<td>146 (±5)</td>
</tr>
</tbody>
</table>

The fractions modern have already been normalized to the $\delta^{13}$C values reported. Errors on the skeletal distance correspond to the drill bit diameter; those on the U-series age estimates correspond to residual error in the age models; those on the fractions modern correspond to the analytical AMS error; and those on the $\delta^{14}$C correspond to the propagated error from all sources. Samples labeled with an asterisk (*) were analyzed at WHOI-NOSAMS, all others at the NSF-Arizona facility.
error of the fractions modern was used to determine the magnitude of the error bars in Fig. 3. Errors were propagated to \(\sigma_{\Delta^{14}C}\) by the standard equation

\[
\sigma_t = \sum_{i=1}^{n} \left( \frac{df}{dx_i} \right) \sigma_{x_i},
\]

where \(f\) is a function of \(n\) variables of \(x\). The resulting expression for \(\sigma_{\Delta^{14}C}\) is

\[
\sigma_{\Delta^{14}C} = 10^{3} \cdot e^{2t} \left( \sigma_{\Delta^{14}C}^2 + \frac{\Delta^{14}C}{r^2} \sigma_d^2 + \frac{\Delta^{14}C}{r^2} \sigma_t^2 \right),
\]

where \(\Delta^{14}C\) is calculated as a function of the fraction modern (Fm), the sclerosponge growth rate \((r, \mu m/yr)\) and the distance from the surface of the sclerosponge from which the subsample was taken \((d, \mu m)\). The mean life of \(^{14}C\), \(\lambda\), is 1/8267. The variable \(t\) is a function of \(d\) and \(r\) that is equal to the number of years before 1950 that the sample was calcified (post-1950 values of \(t\) are less than zero). The error propagated to \(t\) from age model uncertainties and sample increment size can be expressed also by expanding Eq. (1)

\[
\sigma_t = \frac{1}{r} \left( \sigma_d^2 + \frac{d^2}{r^2} \sigma_t^2 \right).
\]

The results of this calculation are shown in Table 2. In the error propagation calculations for the data presented here, the sample increment \((d)\) is slightly larger than estimates of the amount of infilling of basal \(C. nicholsoni\) skeletons \((1 mm [19,27])\). Thus, it is assumed that both infilling and homogenization of coarse samples such as this would not have separable contributions to overall uncertainties. Despite the potentially large magnitudes of \(\sigma_d\), this source of error does not contribute considerably into \(\sigma_{\Delta^{14}C}\) because these age errors are still small compared to the half life of \(^{14}C\). In fact, in young samples \((t < 1000 yr)\), most of the error propagated to \(\sigma_{\Delta^{14}C}\) is from measurement errors in Fm (Fig. 4). Thus, for sclerosponge \(^{14}C\) work, even the most unrefined U-series age models are adequate for sclerosponges that are under 1000 yr in age.

4. Discussion

The data presented here demonstrate the utility of using radio-carbon-independent U-series age models as the basis for oceanographic studies using sclerosponge \(^{14}C\) as a tracer in the N. Atlantic and Caribbean, as has been done in the Pacific [28,29]. In the pioneering Atlantic basin sclerosponge \(^{14}C\) work of Benavides and Druffel [15], there was uncertainty in the \(^{210}Pb\) framework of the bomb curve and the authors ultimately tuned the \(^{210}Pb\) growth rate reasonably to within the confidence interval of the radiocarbon growth rate. Both estimates were very close to the existing growth rate estimates of \(C. nicholsoni\) available at the time [30]. However, the fallible assumption of constant \(Pb/Ca\), as alluded to by the authors, limited the use of \(^{210}Pb\) dating to provide an independent chronology on which to base a detailed study of regional differences in radiocarbon bomb curves that may be related to ocean circulation. It is apparent from new AMS \(^{14}C\) data from Exuma Sound that sclerosponges dated by U-series isotopes constrain the curve, although more data would better support this hypothesis. The data from the TOTO sclerosponge have been troublesome since their analysis several years prior to this work because of the lack of super-modern radiocarbon values in this sclerosponge. At the time of analysis, the NSF-Arizona AMS facility found the sample sizes to be close to the minimum. Both the Arizona and the WHOI facilities have better capabilities for small samples as indicated by the WHOI NOSAMS data in Fig. 4. The new Exuma Sound data trace the mid-20th century radiocarbon increase well enough for further investigation despite inherent uncertainties in U-series age models.

In terms of using sclerosponge \(^{14}C\) to trace the relative contributions of S. Atlantic and N. Atlantic water masses to the SUW, the structure present in the pre-bomb TOTO data indicates that there may be sensitivity to the water mass differences shown in Fig. 1. Unfortunately, what is gained at present in decreasing the analytical error of recently analyzed samples is lost in time domain, so it remains to be seen if the pre-bomb structure in the TOTO data persists upon further analysis of Exuma sclerosponges with more statistical certainty. Neither the data of Benavides and Druffel [15] nor the new data presented here contain very much post-bomb \(^{14}C\) information, however any structure that is present in the earlier portions of the TOTO record would be amplified after 1960. That translates into the possibility of 35 yr of \(^{14}C\) tracer data that can be assessed in relation to the instrumental records of SUW constituents. Both pre-bomb and post-bomb variability in radiocarbon records of this water mass, recorded by sclerosponges, will be invaluable in addressing the question of

![Fig. 4. Error contributions from age models (time), fraction modern, and the quadrature sum of these errors. In most cases, the fraction modern error is the one and only significant contributor to the total uncertainty on the \(^{14}C\) calculation. Sequence numbers can be referenced to Table 2.](image-url)
changes in the contributions of N. Atlantic water into the subsurface Caribbean. Such questions are of growing importance because the subtropical cell circulation and its feedback into the MOC of the N. Atlantic are only recently being realized. Despite the large sample sizes needed for AMS work (relative to stable isotope or minor element proxies) and the infilling of basal aragonite skeletons of sclerosponges, the utility for coupled scleropore–coral radiocarbon studies bracketing the advection of water from the subtropical Atlantic surface to the subsurface of the Caribbean would lie in the ability to constrain decadal scale variation of this convection cell, which has been hypothesized to vary on decadal time scales and longer on based on a short instrumental record. Such a proxy approach to this problem would be unique in its ability to address this hypothesis through procurement of time series of subtropical cell circulation over the time period of anthropogenic perturbation of the carbon cycle and prior.

Acknowledgements

This research was facilitated by the staff of NOSAMS who efficiently and accurately produced results in very rapid turnaround time. The manuscript benefited markedly from the comments of three anonymous reviewers. This material is based upon work supported by the National Science Foundation under Cooperative Agreement OCE-0228996.

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